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(54) A method for the treatment of natural rubber field latex

(57) A method for the treatment of fresh natural rubber field latex comprises incubating the field latex with a proteolytic enzyme at a pH suitable for the enzyme. The amount of enzyme present and the incubation conditions are such that the enzyme-treated field latex, when subsequently processed into epoxidised natural rubber latex, has improved coagulation and crepeing properties.

A method for the preparation of epoxidised natural rubber from fresh natural rubber field latex is also described. This comprises i) incubating the field latex with a proteolytic enzyme at a pH suitable for the enzyme, ii) epoxidising the enzyme-treated field latex to the desired mole % level of epoxidation, iii) coagulating the epoxidised natural rubber latex, and iv) crepeing, washing, crumbling and drying the epoxidised natural rubber.

SPECIFICATION

A method for the treatment of natural rubber field latex

5	This invention relates to the use of natural rubber (NR) field latex for the production of epoxidised natural rubber (ENR). In particular it relates to a method of treatment of NR field latex so that ENR can be prepared from it.	5
10	Epoxidised natural rubber is a relatively new form of rubber which has some useful properties similar to those possessed by more specialised rubbers. For example, depending on the level of epoxidation, it has low gas permeability, good oil resistance, good wet grip, low rolling resistance and high damping. The epoxidation of natural rubber and other unsaturated polymers is well known. ENR may be prepared from centrifuged latex concentrates which is a few weeks old (hereinafter referred to as "matured latex concentrate") by epoxidation with peracetic or performic acid under controlled conditions. After the	10
15	epoxidation reaction, the latex is coagulated and the coagulated rubber is converted to crumbs which are then dried with through circulation of hot air. Since the epoxidation is carried out under acidic conditions, the latex is stabilised with a non-ionic surfactant during the reaction. It is well known that latex stabilised with a non-ionic surfactant during to a temperature close to the cloud point of the surfactant. Large scale production of ENR involves the following steps:	15
20	 (a) epoxidation of the latex, (b) coagulation of the latex with steam, (c) crepeing and washing of the coagulum and hammermilling the crepe to form crumbs, (d) chemical treatment to improve properties, (e) drying of the crumbs and 	20
25	(f) pressing and palleting of the dried crumbs. For the production of 50 mole % epoxidised natural rubber (ENR50) latex from matured latex concentrate it is usual to add 25 parts per hundred parts rubber (phr) of common salt to the latex to lower its colloidal stability before coagulating the latex by passing steam directly into the latex held in containers. This is a batch-wise	25
30	process. The coagulum is allowed to consolidate or mature for 2 hours and then passed through the crepeing mill or a series of crepeing mills. After one pass through the creper, a continuous sheet or crepe is formed. The crepe is usually passed through the creper many times (about 8 times) before it is comminuted to crumbs in a creper-hammermill. These operations, i.e. step (c) of the above process, are important because besides dewatering the coagulum they also facilitate the removal from the coagulum of excess water soluble reactants	30
35	and reaction by-products which, if they were to remain, could cause adverse properties in the rubber. The processing of the ENR50 coagulum into dry crumbs uses the same conventional machinery and equipment as that used for producing crumb rubber e.g. Heveacrumb. However, if the starting material for epoxidation is fresh NR field latex, rather than matured latex concentrate, the ENR latex (ENR50 and ENR25) obtained is very much more difficult to coagulate by heating	35
40	with direct steam even with the addition of common salt. It requires a longer period of heating for coagulation to occur and this gives rise to a lot of very fine particles; however, coagulation is even then still incomplete. After maturation of the coagulum for a few hours or even overnight, the coagulum, on repeated passage through the creper, does not form a crepe but breaks up into small pieces and into fine particles. In fact the coagulum behaves somewhat like a paste. The fine particles can be dispersed in water to give a milky	40
45	dispersion resembling a latex. Hence it is difficult to dewater the coagulum and to wash excess reactants and reaction by-products off the rubber without the loss of a great deal of the rubber itself. Moreover, this paste-like coagulated rubber is difficult to dry. As a result, ENR latex prepared from fresh field latex cannot be economically processed into dry rubber using the conventional rubber processing machinery and equipment. A newer method for coagulating ENR latex, which is infact preferred, is the continuous coagulation method	45
50	using the apparatus and method described in our UK Patent Application No. 8427736. According to this method, ENR latex is passed down a substantially vertical stainless steel column as a thin film on the inner surfaces thereof until it comes into contact with steam which has been introduced into the interior of the column, whereupon the latex is rapidly heated by the steam and coagulates. The resulting coagulum passes through the remainder of the column and is collected at the exit thereof.	50
55	ENR50 latex prepared from matured latex concentrate can be coagulated in the column coagulator but the matured coagulum breaks up into small pieces and into fine particles on the creper. If the small pieces of coagulum are repeatedly passed through the creper, a crepe is formed after 5 to 10 passes through the creper; the finer particles, however, still do not form a crepe. ENR25 latex prepared from matured latex concentrate may also be coagulated by this method and the coagulum can be converted to crepe and crumbs without much	55
60	difficulty. However, in the case of ENR50 or ENR25 latex prepared from fresh field latex, the latex does not coagulate in the column coagulator. Sometimes the latex merely thickens slightly and some flocs are formed which even on maturation behave somewhat like a paste and do not form a crepe even on repeated passage through the creper.	60
65	In many rubber-producing countries, it would be more economical to use fresh field latex instead of matured latex concentrate as the starting material from which ENR is prepared. However, in view of the aforementioned problems this has so far not been possible. These problems are rather unique and it is believed that difficulties	65

65 problems this has so far not been possible. These problems are rather unique and it is believed that difficulties

of a similar nature have not been encountered before in the processing of natural rubber latex into dry rubber. It is to be understood that the term "field latex" as used herein includes field latex in which the bottom fraction and sludge have been removed by clarifying with a centrifugal clarifier. There are a number of differences between fresh field latex and matured latex concentrate, such as a

difference in particle size. However, it may be supposed that for present purposes the most important difference is the presence of a much larger amount of non-rubber substances in field latex. There are a lot of non-rubber substances in natural rubber latex including the following classes of substances: inositols, carbohydrates, proteins, lipids, amino acids, other organic acids, nitrogeneous bases, thiols, nucleic acids and metallic cations and inorganic anions. It may seem obvious to try to solve the problems by removing the 10 non-rubber substances, but it is not at all obvious as to which of these are causing the problems.

British Patent No. 1,366,934 describes a method of removing protein from natural rubber which comprises incubating natural rubber latex with a proteolytic enzyme at a pH suitable for the enzyme in the presence of a soap to prevent premature thickening or coagulation of the latex and subsequently separating proteinaceous material from the rubber. The resulting deproteinised natural rubber (DPNR) contains not more than 1% of proteinaceous material.

It has now been found that the afore-mentioned problems associated with the use of fresh field latex for the production of epoxidised natural rubber are caused by the presence of a large amount of protein in the field latex and, more specifically, it is the molecular size of the proteins which causes the problems.

According to the present invention there is provided a method for the treatment of fresh natural rubber field 20 latex which comprises incubating the field latex with a proteolytic enzyme at a pH suitable for the enzyme, the amount of enzyme present and the incubation conditions being such that the enzyme-treated field latex, when subsequently processed into epoxidised natural rubber latex, has improved coagulation and crepeing

According to a further embodiment of the present invention there is provided a method for the preparations 25 of epoxidised natural rubber from fresh natural rubber field latex which comprises the following steps:i) incubating the field latex with a proteolytic enzyme at a pH suitable for the enzyme, ii) epoxidising the enzyme-treated field latex to the desired mole % level of epoxidation, iii) coagulating the epoxidised natural rubber latex, and iv) crepeing, washing, crumbling and drying the epoxidised natural rubber. The latex to be treated with enzyme could also be skim latex or field latex to which some skim latex has been

added before epoxidation. It has been found that a limited enzyme treatment of fresh or matured latex concentrate before epoxidation

to high epoxidation levels (e.g. ENR 50) enables the epoxidised latex to be coagulated using either the batch coagulation method or the continuous column coagulation method without the need to add common salt to 35 the latex and the resulting coagulum has good crepeing properties.

The present invention therefore provides a way of overcoming the previously described problems by providing a method of reducing the size of the protein molecules in the field latex by enzymatic hydrolysis using any proteolytic enzyme. The level of enzyme added to the field latex and the incubation time are very important and are much greater than those required for preparing enzyme deproteinised natural rubber by the previously known method referred to above. After the enzyme treatment, it is not necessary to remove the degraded protein fragments from the latex. The enzyme-treated field latex, after the appropriate incubation period, is ready for epoxidation to the required mole % epoxidation level. The ENR latex thus prepared can be successfully coagulated by steam according to either (a) the batch coagulation method, or (b) the continuous coagulation method. In both processes of coagulation, no addition of common salt to the latex is required.

In the batch coagulation method, steam is passed directly into the ENR latex held in a series of containers until the temperature reaches about 98°C. The hot coagulum is left to mature typically for from about 1/2 hour to 3 hours. During this period the smaller pieces of coagulum consolidate and form a big and quite coherent with mass. Coagulation is completed giving a clear serum. During the maturation period, the coagulum is tested at intervals for its ability to form a crepe after one pass through the creper. As soon as this is possible the

50 coagulum is creped and washed about 8 times and is then comminuted to crumbs using the creper-hammermill. For the final size-reduction other conventional machinery, e.g. a creper-shredder or extruder or pelletiser, may also be used. The crumbs are then dried with through circulation of hot air (about 80°C to 100°C) in the usual way. It is not advisable to leave the hot coagulum to mature for longer than is necessary as excessive heat is known to degrade the rubber molecules. Maturation of the hot coagulum for different periods of time may be used to prepare ENR of varying molecular weight and hence generally

different Mooney viscosity.

In the continuous coagulation method, the ENR latex is passed down a vertical stainless steel column and is coagulated with steam inside the column as described earlier. The coagulum is collected in a container placed at the exit of the column. It is then left to mature typically for from 1/2 hour to 3 hours and is then creped and 60 washed and converted to crumbs and dried in a similar way as in the batch coagulation method. For this method to work effectively, it is desirable for the ENR latex to have a dry rubber content of about 25% or higher.

In the present process, we have used Savinase 8.0L and Alcalase 2.5L both of which are alkaline proteinases but other proteolytic enzymes may be used. Both these enzyme preparations are commercially available. These are supplied in liquid form and consist of the active enzyme dissolved in a solvent system consisting of 65 1,2-propanediol, stabiliser and water. Savinase 8.0L has an activity of 8.0 Kilo Novo Proteinase Units per gram

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(KNPU/g) while Alcalase 2.5L has an activity of 2.5 Anson Units per gram (AU/g).

The physical form of the enzyme is not important, for example Alcalase 2.0T which is available as dry granules having an activity of 2.0 AU/g has also been used successfully. A disadvantage of using the granular form is that the inert carrier, e.g. titanium dioxide, which is insoluble in water must be removed by sedimentation or centrifugation after the enzyme has been dissolved. This operation results in the loss of some of the enzyme. Moreover, if sedimentation is used to remove the inert carrier, a dilute solution of about 5% must be prepared to obtain maximum recovery of the enzyme solution. This dilute enzyme solution causes undesirable dilution of the field latex.

The amount of enzyme may be chosen to obtain a desired rate or degree of proteolysis. We have used 0.05 to 1 phr of the liquid enzyme for fresh field latex. Time and temperature of incubation may also be chosen to achieve the desired rate and degree of proteolysis, typical figures being from 12 to 96 hours at from 25°C to 60°C. The pH range for the enzymes is from 7.5 to 11.0. It will be appreciated that if the enzymatic hydrolysis is carried out at a high temperature (40-60°), the incubation time and/or the level of enzyme required can be reduced.

The amount of enzyme and the time of incubation are very important. Low levels of enzyme and short incubation times which are sufficient for preparing DPNR are inadequate for solving the problems of coagulation and crepeing satisfactorily. These are illustrated in Examples 1 to 3. For the preparation of DPNR as described in British Patent No. 1,366,934 the latex after incubation with enzyme is diluted to a solids content of about 3% prior to coagulation with acid so as to avoid entrapping proteinaceous material in the coagulum.

20 We have used this method to assess approximately the extent of protein breakdown using different levels of enzyme and different incubation times. This is illustrated in Example 1. The nitrogen content of the DPNR provides some indication of the extent of protein breakdown.

The ENR produced from enzyme-treated field latex has a low nitrogen content, typically about 0.04% on the weight of the rubber. This value is even lower than the lowest value obtained, about 0.06%, for DPNR prepared by enzyme deproteinisation of field latex (Example 1). The reason for this is probably due to further hydrolysis of the enzyme-degraded protein fragments and/or hydrolysis of other nitrogen-containing compounds (e.g. phospholipids) under the conditions of the epoxidation reaction, i.e. heat and performic acid. The increased solubility of the protein fragments during the heat coagulation of the ENR latex could also account for this lower value. The ash content of the ENR is typically 0.08% by weight. It is noted that the nitrogen content of ENR prepared from matured latex concentrate is about 0.11% on the weight of the rubber.

If it is desired to improve the properties of the ENR e.g. Wallace plasticity and plasticity retention index, this may be achieved using known chemical methods. For example an antioxidant may be added to the latex before coagulation and the ENR crumbs may be treated with an antioxidant before drying.

It is not fully understood why enzymatic hydrolysis of the proteins in field latex should solve the problems of difficulty in coagulation of ENR latex and inability of the coagulum to form a crepe, but it seems likely that the following factors contribute to the result. Under the epoxidation conditions which consist of heating the latex with formic acid and hydrogen peroxide in the presence of a non-ionic surfactant, (a) the protein molecules are chemically converted to some form of steric stabiliser and/or (b) the protein molecules interact chemically with the non-ionic surfactant to form bigger steric stabiliser molecules. (Non-ionic surfactants are steric stabilisers

themselves). These protein-derived steric stabiliser molecules have the effect of inhibiting or reducing the probability of the latex particles cohering and coalescing with one another to form a quite continuous and coherent mass, when collision between particles occurs at temperatures of less than about 100°C. Hence the ENR latex is difficult to coagulate by heating with steam. In the presence of salt the protein-derived steric stabiliser and the non-ionic surfactant gradually lose some of their stabilisation property towards heat. Hence on heating the ENR latex in the presence of common salt, some coagulation occurs; this is the result of rubber

on heating the ENR latex in the presence of common salt, some coagulation occurs; this is the result of rubber particles coalescing to form loose aggregates. Depending on the size, each loose aggregate contains many rubber particles having some contact with one another but because of the presence of the protein derived steric stabiliser molecules on the surface of the particles, the latter are inhibited or hindered from further coalescing with one another to form a bigger and quite continuous and coherent mass. The loose aggregates
 are also similarly inhibited or hindered from coalescing with one another to form a bigger mass. In fact the matured coagulum on passing through the creper breaks up into loose aggregates.

When the protein molecules are hydrolysed into small fragments e.g. polypeptides and amino acids and under the epoxidation reaction conditions, the reaction products that may be formed from these small fragments have a lower steric stabilisation property compared with the very much bigger protein-derived steric stabiliser; the smaller the fragments, the lower is the stabilisation property. This probably explains why a higher level of enzyme and longer incubation time which result in a greater degree of proteolysis are more effective in solving the problems described.

The following examples are included to illustrate the present invention.

60 Example 1

Field latex was preserved with 0.25% ammonia on latex weight. Potassium cleate was added to the latex at a level of 1 phr to stabilise the latex when the proteins were degraded. The enzymes, Savinase 8.0L and Alcalase 2.5L, were aded to two samples of the latex at levels of 0.1 to 0.5 phr and the latex mixtures were incubated at room temperature (about 30°C) for 1 to 6 days.

456 After various incubation periods, a sample of each latex was diluted to a solids content of about 3% before

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coagulation with formic acid in the usual way. The coagulated rubber was creped and dried in warm air in the usual way. The nitrogen content of the rubber is given in Table 1.

TABLE 1 Nitrogen content of rubber (weight %) from field latex treated with Savinase and Alcalase

5	I ABLE 1 Nitroger	n content d	or rubber ·	(weight	%) Trom T	ieia iatex ·	treated with Savi	nase and Alcalas	. ·	5
ŭ	Enzyme level, phr									
	Days	0.10	0.15	0.20	0.30	0.40	0.50	٠		•
10	1	0.08 (0.25)	0.09 (0.13)	0.08 (0.09)	0.08 (0.10)	0.06 (0.08)	0.08 (0.10)			10
:	2	0.09 (0.09)	0.08 (80.0)	0.07 (0.09)	0.08 (0.09)	0.06 (0.07)	0.07 (0.07)			
15	3	0.07 (0.08)	0:06 (0.07)	0.06 (0.07)	0.06 (0.06)	0.06 (0.06)	0.07 (0.07)			15
20	4	0.07 (0.07)	0.07 (0.07)	0.07 (0.07)	0.07 (0.06)	0.06 (0.07)	0.07 (0.06)		; · · · · · · · · · · · · · · · · · · ·	. 20
	6	0.07 (0.06)	0.07 (0.07)	0.06 (0.07)	0.07 (0.08)	0.07 (0.08)	0.06 (0.07)			
25	Unbracketed values are for Savinase treated latex while bracketed values are for Alcalase treated latex. Nitrogen content of control rubber (i.e. no enzyme treatment) = 0.35% It is seen that for an incubation time of 1 day and at enzyme levels of less than about 0.2 phr, Savinase 8.0L is more effective than Alcalase 2.5L but at longer incubation times both enzymes are equally effective in hydrolysing the proteins in the latex.							25		
30	Example 2 Fresh field lates	x was pres	erved wi	th 0.25%			nonia (System A) o D) and 0.013% of z			30
35	Preservative syst surfactant (e.g. To phr. (Teric 16A29	em B is kn eric 16A29 is a conde	own to ke) used to nsation p	eep field stabilise product o	latex stal the latex of one mo	ole and fl for the e decule of	uid for a longer pe poxidation reaction a long chain aliph he liquid enzyme p	riod than system on was added at a atic alcohol mai	A. Non-ionic a level of 2 nly cetyl	35
40	latex was epoxidi reaction was then steam by either (a	ised to ENI n stopped I a) the batcl	R50 by he by neutra h coagula	eating wi alising th ation me	th formic e acid wit thod or (t	acid and th ammo o) the cor	perature for 24 to 6 I hydrogen peroxio nia. The ENR50 lat Itinuous coagulati	de for about 24 h tex was then coa on method.	ours. The gulated with	40
45	temperature read 1/2 hour to 3 hour	ched about s until it co d then size th circulati	t 95°C. Th ould form -reduced	e latex con a crepe to crum	oagulate d after on os on the	d and the le pass th creper-h	into the latex in a second unit was less to	ft to mature typic It was then crepe	ally for about and washed	45

In the continuous coagulation method, the ENR50 latex was passed down a vertical stainless steel column as a thin film and was coagulated with steam inside the column as described in UK Patent Application No. 8427736. The coagulum was collected in container placed at the exit of the column. It was then left to mature typically for 1/2 hour to 3 hours and was creped and washed 8 times and converted to crumbs and dried in a similar way as for the batch coagulation method. For this method to work effectively it is desirable for the

ENR50 latex to have a dry rubber content of about 25% or more.

The conditions for enzyme treatment and their effect upon the coagulation of ENR50 latex and the ability of the coagulum to form a crepe are shown in Table 2.

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TABLE 2 Effect of enzyme treatment conditions on the coagulation and crepeing of ENR50

		Experimental	Enzyme	Incubation	•					
		field latex	level,phr	Time,hour		on Crepe	ina .			
5				, -,	J		9	5		
	1.	System A	Nil		poor	canno	tform	•		
					•	crepe				
	2.	System A	0.40 Savinase	24	good	poor				
	3.	System A	0.25 Savinase	42	good	poor				
10	4.	System A	0.25 Savinase	66	good	good		10		
	5.	System A	0.25 Alcalase	66	good	good				
	6.	System B	0.35 Savinase	42	good	good				
	7.	System B	0.35 Alcalase	42	good	good				
						_				
15	Go	ood coagulation is	ndicates that com	plete coagulat	ion occurred, whi	ile poor coagu	lation indicates that	15		
		agulation was eit				_				
							creper, while poor			
		epeing indicates t								
							eriments (2) to (7). These			
20							natured latex concentrate or	20		
							verage ash content of the			
			 prepared accord 	ding to Experim	ients (4) to (7) wa	s 0.08% by we	ight with a standard			
		viation of 0.02%.	_							
		It is seen that the p		all amount of Ti	MTD and zinc oxid	de in the latex	did not affect the			
25		ectiveness of the						25		
							n are very important in order			
	to	solve the problen	ns of coagulation	and crepeing s	atisfactorily. Low	levels of enzy	me and short incubation			
		nes which are suff	licient for prepari	ng DPNR (Table	e 1) are inadequa	te for solving t	hese problems			
20	sa	tisfactorily.					•			
30	Ev	ample 2						30		
	Example 3 Fresh field latay was preserved with 0.25% by weight of ammonic and stabilized with 1.6 phr of non-ionic									
	CII	Fresh field latex was preserved with 0.25% by weight of ammonia and stabilised with 1.6 phr of non-ionic surfactant (e.g. Teric 16A29) and then treated with Savinase 8.0L. After incubation the latex was epoxidised to								
	FN	IR25 by heating w	ith formic acid ar	nd hydrogen ne	rovide for about '	24 hours The	reaction was then stopped			
35	by	neutralising the a	ocidic latev mivtu	re with ammon	is The laterwas	coagulated w	ith steam by either (a) the	35		
	ba	tch coagulation n	nethod or (b) the	rontinuous coa	aulation method	and the coad	ilum was creped and	35		
	CO	nverted to crumb	s and dried in a si	milarway as fo	r ENR50 in Evami	nie 2 The initi	al sizes of the rubber flocs			
	ap	peared to be sma	ller than those of	FNR50 Howey	er, on maturation	for 1/2 hours	o 2 hours, these flocs			
	CO	nsolidated into a	big mass which c	ould be creped	and converted to	crumbs with	out problems if enzymatic			
40		drolysis was suffi						40		
				me treatment c	n the coagulation	n of ENR25 lat	ex and crepeing behaviour			
		the coagulum is s		•						
				-			· · · · · · · · · · · · · · · · · · ·			
	TA	BLE 3 Effect of en	zyme treatment d	conditions on th	ne coagulation an	d crepeing of	ENR25			
45		•					11:	45		
			•	cubation	•		•	÷		
	Ex	periment lev	vel,phr Ti	ime,hours	Coagulation	Crepeing	4 · · · · · · · · · · · · · · · · · · ·			
	_			_						
	1	0.3		=	poor	:	The second state of the second			
50		0.4		3 .	poor		The first of the state of the s	50		
	3	0.6			good	good.	*	1.45		
	4	0.4	10 96	•	good	good	to the typical of the first section of			

The nitrogen content of the ENR25 obtained was 0.04 weight % for Experiments (3) and (4) and the ash content 55 was similar to those of ENR50 in Example 3.

Example 4

This example demonstrates heat accelerated enzymatic hydrolysis.

The incubation time and/or the level of enzyme needed can be reduced by accelerating the enzymatic

60 hydrolysis of the proteins present in field latex. This is achieved by carrying out the hydrolysis at elevated temperature (e.g. 40°C – 60°C). It has been found that it is not necessary to maintain the temperature of the enzyme-treated latex at a constant level. Hence on day zero 4000 litres of enzyme-treated field latex (treated in a similar way as in Example 2 for ENR 50 and Example 3 for ENR 25) were heated to 55°C, whereupon the heating was discontinued to save energy (and thus reduce costs). The latex mixture was covered and left

65 undisturbed overnight (about 18 hours) so that the hydrolysis could proceed. The next day (day one) the

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temperature of the latex was found to have dropped to about 46°C. At the end of this 18 hour enzyme treatment, the latex was ready for epoxidation to ENR 50 in a similar way as in Example 2.

For a 42 hour enzyme treatment, the latex was again heated to 55°C on day one, whereupon the heating was discontinued and the latex left undisturbed for 24 hours. It was then epoxidised to ENR 50 in a similar way as in Example 2 or epoxidised to ENR 25 as in Example 3.

Similarly for a 66 hour enzyme treatment, the latex was again heated to 55°C on day two, the heating was then discontinued and the latex left for another 24 hours. It was then epoxidised to ENR 25 in a similar way as in Example 3.

The epoxidised latex, after neutralisation with ammonia, was coagulated with steam by either (a) the batch coagulation method or (b) the continuous column coagulation method and the coagulum was creped and converted to crumbs and dried in a similar way as in Example 2.

The effects of the above conditions of heat and enzyme treatment on the coagulation of epoxidised latex and the crepeing behaviour of the coagulum are shown in Table 4.

15 TABLE 4: Effect of enzyme treatment conditions (45° – 55°C) on the coagulation and crepeing of ENR 50 and ENR 25

	5	Enzyme level,	Incubation	C	0	
	Experiment	phr	Time, hours	Coagulation	Crepeing	
20		•	_			20
	1. ENR 50	0.25 Alcalase	18	Good	Poor	•
	2. ENR 50	0.40 Alcalase	18	Good	Good	
	3. ENR 50	0.40 Savinase	18 .	Good	Good	
	4. ENR 50	0.20 Alcalase	42	Good	Poor	-
25	5. ENR 50	0.30 Alcalase	42	Good .	Good	25
	6. ENR 50	0.30 Savinase	42	Good	Good	
	7. ENR 25	0.55 Alcalase	42	Good	Good	:
	8. ENR 25	0.35 Alcalase	66	Good	Good	•
	9. ENR 25	0.35 Savinase	66	Good	Good	
30	· .		•			30

Alcalase refers to Alcalase 2.5 L while Savinase refers to Savinase 8.0. L.

For ENR 25, the coagulation of the epoxidised latex (Experiments 7 to 9) was much better than that in Experiments 3 & 4 of Example 3 since the initial sizes of the coagulated rubber appeared to be bigger and therefore the coagulum could be creped in a shorter time.

35 The nitrogen and ash contents of the epoxidised rubbers were similar to those in Examples 2 & 3.

CLAIMS

- A method for the treatment of fresh natural rubber field latex which comprises incubating the field latex
 with a proteolytic enzyme at a pH suitable for the enzyme, the amount of enzyme present and the incubation conditions being such that the enzyme-treated field latex, when subsequently processed into epoxidised natural rubber latex, has improved coagulation and crepeing properties.
 - 2. A method as claimed in claim 1, wherein the natural rubber field latex is incubated with from 0.05 to 1 phr of a proteolytic enzyme having an activity of 8.0 KNPU/g enzyme of 2.5 AU/g enzyme for from 12 to 96 hours at from 25°C to 60°C.
 - 3. A method as claimed in claim 1 or claim 2, wherein Savinase or Alcalase or other alkaline proteinase is used as the enzyme at a pH of from 7.5 to 11.
 - 4. A method as claimed in any one of claims 1 to 3, wherein a non-ionic surfactant is present at a level of from 1 to 5 phr so to stabilise the latex during the enzyme treatment and prevent premature coagulation.
- 50 5. Epoxidised natural rubber latex which has been prepared from natural rubber field latex treated according to the method as claimed in any one of claims 1 to 4.
 - 6. A method for the preparation of epoxidised natural rubber from fresh natural rubber field latex which comprises the following steps:
 - i) incubating the field latex with a proteolytic enzyme at a pH suitable for the enzyme,
- 55 ii) epoxidising the enzyme-treated field latex to the desired mole % level of epoxidation,
 - iii) coagulating the epoxidised natural rubber latex, and
 - iv) crepeing, washing, crumbling and drying the epoxidised natural rubber.
 - 7. A method as claimed in claim 6, wherein the epoxidation of step ii) is performed by heating the enzyme-treated field latex with formic acid and hydrogen peroxide.
- 8. A method as claimed in claim 6 or claim 7, wherein the coagulation of step iii) is performed by passing steam directly into the epoxidised natural rubber latex until the temperature reaches about 98°C.
 - 9. A method as claimed in claim 6 or claim 7, wherein the coagulation of step iii) is performed by passing the epoxidised natural rubber latex down a stainless steel column counter-current to steam.

- 10. A method as claimed in any one of claims 6 to 9, wherein additional chemicals, such as an antioxidant, are added to the epoxidised natural rubber latex before coagulation and/or to the epoxidised natural rubber crumbs before drying.
- 11. Epoxidised natural rubber which has been prepared from natural rubber field latex treated according to the method as claimed in any one of claims 1 to 10 and wherein the nitrogen content is not more than 0.08% by weight.

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